

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Appl. No : 10/596,489 Confirmation No. : 7292  
Applicant : Abdur-Rashid, Kamaluddin  
Filed : December 15, 2004  
Title : Asymmetric Imine Hydrogenation Processes  
TC./A.U. : 1621  
Examiner : Nwaonicha, Chukwuma O  
Docket No. : 14696-13

Honorable Commissioner for Patents  
P. O. Box 1450  
Alexandria, Virginia 22313-1450

Dear Sir:

**DECLARATION UNDER 37 CFR §1.132**

I, Kamaluddin Abdur-Rashid, a citizen of Canada, and resident of Mississauga, Ontario, Canada, declare that the following facts are within my knowledge and are true.

1. I reside at 3414 Joan Drive, Mississauga, Ontario, Canada L5B 1T5.
2. I am the inventor and owner of the subject matter as claimed in U.S. Patent Application No. 10/596,489 filed December 15, 2004 (hereafter "the Application").
3. I have read and understood the Office Action that issued for the Application on August 3, 2009. The Examiner is of the view that claims 1, 3, 5-15, 16-19 and 25-53 are obvious in light of Cobley et al. (US 6,528,687) in view of Abdur-Rashid (WO 03/097571).
4. I herein enclose photocopied pages of my laboratory notebook containing pages 1-70. I submit that this notebook contains experimental data which forms the basis for the subject matter of the claims of the Application. I note that the



notebook also contains experimental data that is not related to the subject matter of the Application.

5. I respectfully submit that the first day on which an imine falling within the scope of formula I in the Application was successfully hydrogenated using the process of the Application, is after the date on which Abdur-Rashid was assigned to myself. I note that this experiment is found on page 52 of my notebook.

6. I therefore submit that the date the present invention was made is after the date of assignment of the prior art reference Abdur-Rashid to myself.

7. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statement and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the Application or patent resulting therefrom.

Date

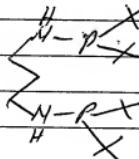
October 30 2009

  
Kamaluddin Abdur-Rashid

Preparation of  $\sum_{H}^{N-PhBu_2}$

A solution of 1,3-diamino propane (3.72g, 50 mmol) in toluene (25 ml) was added dropwise to a solution of di-tert-butylphosphine chloride (9.03g, 50 mmol) in 50 ml toluene. The mixture was refluxed for 4 hours under argon. The ammonium chloride salt was removed by filtration through a sintered glass filter. The solvent was removed under vacuum and the product purified by distillation under vacuum.

yield = 6.62g



:PN(CN)P

~~[REDACTED]~~ Reaction of  $\text{RuCl}_2(\text{p}-\text{cymene})$  + PNCNP

A mixture of 15mg  $\text{RuCl}_2(\text{p}-\text{cymene})$  and PNCNP (18mg) and  $\text{NEt}_3$  (10mg) was refluxed in 0.6g of  ${}^2\text{BuOH}$ . The NMR spectrum showed the formation of two isomers of the olefin complex, the alkylidene complex + a degradation compound? There was some degradation of the ligand to generate a broad singlet at 8152.1 $\delta$

NB - No reaction at room temperature

~~[REDACTED]~~ A mixture of  $\text{RuCl}_2(\text{p}-\text{cymene})^{15\text{mg}}$ , PNCNP (18mg) and  $\text{NEt}_3$  (10mg) and  ${}^2\text{PrOH}$  (1 drop) was heated to 110°C in toluene (0.6g). The NMR showed no formation of the olefin isomers, the alkylidene complex, and several degradation compounds, including byproduct of the ligand.

~~[REDACTED]~~ A mixture of  $(\text{RuCl}_2(\text{cod}))_2$  (10mg), PNCNP (18mg),  $\text{NEt}_3$  and  ${}^2\text{PrOH}$  (1 drop) was warmed at 60°C in toluene for several hours. The NMR spectrum showed the formation of the above-mentioned products in addition to degradation species.

Reaction of BuLi(*p*-cymene) + PNCNP  
A mixture of BuLi(*p*-cymene) (13 mg),  
PNCNP (18 mg) and butidine (10 mg) was  
warmed at 60 °C in toluene. The  
<sup>1</sup>H NMR spectra showed the formation of  
the olefin isomers, alkylidene and ~~an~~<sup>new</sup>  
unknown compound. The mixture was  
refluxed overnight. Several degradation  
products was observed by <sup>1</sup>H NMR.

A mixture of BuLi(*p*-cymene) (15 mg), PNCNP (10 mg)  
butidine (10 mg) was warmed at 60 °C in <sup>1</sup>H NMR  
(18.6 g). The <sup>1</sup>H NMR spectra showed the gradual  
formation of the olefin, alkylidene and  
unknown compound. The mixture was  
heated at 80 °C overnight. The <sup>1</sup>H NMR  
spectrum showed the new compound  
as the main product. It seems to  
relatively insoluble. The mixture  
was filtered, washed with 1 ml  
methanol and <sup>the soln</sup> dried. ~~It is~~ <sup>the</sup> soln  
were redissolved in CD<sub>2</sub>Cl<sub>2</sub>  
(sparingly soluble). The <sup>1</sup>H NMR spectrum  
showed this as the main compound,  
in addition to the olefin, and  
alkylidene.

## Reaction of $\text{BuLi}(\beta\text{-cymene}) + \text{PNCNP}$

$\text{BuLi}(\beta\text{-cymene})$  (15 mg), PNCNP (18 mg) and  $\text{NEt}_3$  (10 mg) was warmed in  $^+{\text{BuOH}}$  at  $60^\circ\text{C}$ . The NMR spectrum showed the formation of the olefins, alkylidene and new complexes. The mixture was warmed overnight at  $100^\circ\text{C}$ . There was 35% consumption of the ligand. Only small amount of the degradation byproduct of the ligand ( $\text{C}_2\text{H}_4$ ) at  $\delta 152$  was observed.

$\text{BuLi}(\beta\text{-cymene})$  (15 mg), PNCNP (18 mg) and  $\text{NEt}_3$  was warmed in toluene at  $60^\circ\text{C}$ . The NMR spectrum showed the slow formation of the olefins and alkylidene and very little trace of the new compound. The mixture was left standing overnight at  $60^\circ\text{C}$ . The NMR spectrum showed 40% consumption of the ligand.

Reaction of  $\text{BuLi}(\text{p-cymene}) + \text{PhCNP}$ .

A mixture of  $\text{BuLi}(\text{p-cymene})$  (15mg),  $\text{PhCNP}$  (18mg) and  $\text{NET}_3$  (10mg) was warmed in toluene (0.6g) at  $80^\circ\text{C}$ . The NMR spectrum showed a gradual ~~formation~~ of the olefins, alkyldene and new (Lw) compounds. The reaction was 90% completed after 1 hour and 20 minutes.

A mixture of  $\text{BuLi}(\text{p-cymene})$  (15mg)  $\text{PhCNP}$  (18mg) and  $\text{NET}_3$  (10mg) was heated at  $80^\circ\text{C}$  in  $^t\text{BuOH}$  (0.6g). The NMR spectra showed gradual formation of the 4 main products. The reaction was 95% completed ~~at~~ 2½ hours, however, there was some formation of the ligand degradation product at 81.82 (31P). The reaction mixture was allowed to stand at  $60^\circ\text{C}$  overnight, then filtered, the solids washed with methanol and redissolved in  $\text{CH}_2\text{Cl}_2$ . The NMR spectrum showed approximately 60% of the new complex along with the olefins, and alkyldene.

## Reaction of BuLi(*p*-cymene) + PNCNP.

A mixture of BuLi(*p*-cymene) (1.5 mg), PNCNP (18 mg) and  $\text{NET}_3$  (8 mg) was warmed at  $80^\circ\text{C}$  in  $\text{P}_2\text{O}_4\text{H}$  (no reaction at room temperature). The NMR spectrum showed the gradual formation of the various products along with a species at  $\delta 112$  ( $^3\text{P}$ ) and  $\delta 8-15.8$  ( $^1\text{H}$ ), which may be the dihydride. There was also a gradual formation of a green ppt, which coats the inside of the NMR tube.

## Reaction of BuLi(*p*-cymene) + PNCNP Preparative reaction.

A mixture of BuLi(*p*-cymene) (1.5 g), PNCNP (1.8 g) and  $\text{NET}_3$  (0.50 g) ~~in~~  
toluene (10 ml) was warmed for  $1\frac{1}{2}$  hour at  $80^\circ\text{C}$ . The NMR spectrum of the mixture showed complete formation of the olefin isomers, alkylide and new compounds. The solvent was reduced to in volume to 2 ml, during which there was a precipitation of an orange solid. This was filtered, washed with methanol and dried under vacuum. The mother liquor and washings were evaporated to dryness. 3 ml of methanol was added and the mixture stirred for 30 minutes. The solids were filtered, washed with

347 ml methanol and dried under vacuum. The combined yield = 1.844 g.

[REDACTED] A third crop (115 mg) was obtained from the mother liquor which was left standing in the refrigerator ( $75^{\circ}\text{C}$ ) for 1 week.

Combined total yield = 1.957 g.

[REDACTED] Reaction of RuHCl (PNP) complexes with  $\text{H}_2$ : 15 mg of the mixture of complexes was dissolved in toluene- $d_6$  (0.6 g) in a Young NMR tube and the solution exposed to an atmosphere of  $\text{H}_2$  gas. The NMR spectrum shows the clear formation of the dihydride complex.

[REDACTED] The solution of the dihydride complex was exposed to Argon gas after 3 freeze-pump-thaw cycles. There was very slow conversion of the dihydride complex; only 10% change after 24 hours and 15% after 5 days.

[REDACTED] Upon heating a suspension of the olefin and allylidene RuHCl (PNP) complexes in toluene- $d_6$ , a new complex (18-22.23 hydride region) constituted the main species. This new complex seems to be in equilibrium with the olefin and allyl toluene complexes.

Sublimation of  $\text{ReHCl}(\text{PNNA})$  complexes.

100 mg of a mixture of the olefin and allylidene complexes was sublimed under vacuum at  $210^\circ\text{C}$ . The NMR spectrum of the residue shows mainly the new compound (89%) along with the olefin and allylidene complexes.

Exposure of a solution of the new compound to  $\text{H}_2$  gas resulted in the formation of  $\text{RuH}_2\text{Cl}(\text{PNCPN})$ .

Preparation of  $\text{RuCl}(\text{CO})_2(\text{PNCPN})$

A solution of the  $\text{ReHCl}(\text{PNNA})$  complexes (100 mg) was dissolved in 10 g of pyridine and the resulting solution flushed under an atmosphere of  $\text{CO}$  gas for 1 hour. The solvent was removed under vacuum, to give a tan-colored residue. Yield = 108 mg.

Preparation of  $\text{RuCl}(\text{CO})(\text{PNCPN})$

100 mg of the dianionyl complex was refluxed for 4 hours in toluene under argon. The solvent was then removed under vacuum, resulting in an orange residue. Yield = 92 mg.  $\nu_{\text{CO}} = 1899 \text{ cm}^{-1}$

The "new compound" was determined to be the Fischer carbene complex:



Reaction of  $\text{RuH}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)$  with  $\text{H}_2\text{Si}(\text{Ph})$ .



$\text{H}_2\text{Si}(\text{Ph})$  (2 mg) was added to a solution of  $\text{RuH}(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)$  (2.2 mg) in  $\text{Ca}(\text{D}_6)$  (0.6 g). The NMR spectrum showed a mixture of products.

Reaction of  $\text{RuHCl}(\text{P}(\text{C}_6\text{H}_5)_3)$  complex with  $\text{PMe}_3$ . The mixture of olefin complexes (25 mg) in  $\text{Ca}(\text{D}_6)$  and  $\text{PMe}_3$  (20 mg) formed a clear solution as soon as it was prepared. The NMR spectrum showed the formation of  $\text{RuHCl}(\text{PMe}_3)_4$ .

Reaction of  $\text{RuHCl}(\text{PNMe}_2)$  with  $\text{PMe}_3$ .

A mixture of the complexes (25 mg) and  $\text{PMe}_3$  (20 mg) in  $\text{Ca}(\text{D}_6)$  resulted in a clear solution instantaneous due to the formation of  $\text{RuHCl}(\text{PMe}_3)_4$ .

Reaction of  $\text{Cp}^*\text{Rh}(\text{cod})\text{Cl}_2$  with PNCPN

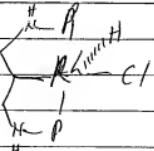
A mixture of  $\text{Cp}^*\text{Rh}(\text{cod})\text{Cl}_2$  (15mg), PNCPN (20mg) and 0.5g of cod<sub>6</sub> was prepared. <sup>in an NMR tube</sup> Two new species (<sup>31</sup>P) were observed after 20 minutes at room temp.

The sample was heated for 20 minutes at 80°C under H<sub>2</sub> gas. A new species at 126.8 ppm (<sup>31</sup>P) appeared.

The sample was refluxed for 1 hour. The conc. of new complex increased to formation of a bright yellow ppt.

The solvent was decanted (from above), the solid washed dissolved in cod<sub>6</sub> (warm). Only one species present (NMR).

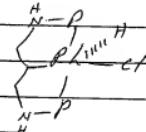
The reaction was repeated in iPrOH under H<sub>2</sub> gas. The solvent was decanted, the residue dried and dissolved in CD<sub>2</sub>Cl<sub>2</sub>. NMR showed same complex at 126.8 ppm (<sup>31</sup>P).



Equilibrium reaction of  $\text{Ph}_2\text{CH}(\text{C}_6\text{H}_5)\text{P}(\text{NHCNP})$  gives 10 mg of a sample consisting mainly of the Fisher carbene complex (72 %) was ~~obtained~~ prepared by shaking in  $(\text{D}_2\text{C}_6\text{H}_5)$  (0.8 g), filtering the solution and run the work. It consists of Fisher carbene (72.35 %), anti olefin (13.47 %), syn olefin (11.66 %) and Schrock carbene (2.52 %). The solution was left standing at room temperature.

After 48 hours (13/11/02) the NMR showed Fisher carbene (36.49 %), anti olefin (21.39 %), syn olefin (40.26 %) and Schrock carbene (1.86 %).

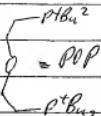
Preparation of



A mixture of  $(\text{Et}_2\text{O})_2\text{AlCl}_3$  (150 mg) and PNCNP (200 mg) in 2-propanol (2 ml) was refluxed for 2 hours under  $\text{H}_2$  gas. The mixture was cooled to room temp., filtered, the solids washed with 2-propanol (0.5 ml), MeCO (1.0 ml), and dried under vacuum.

yield = 282 mg.

## Reaction of $\text{RhCl}_3(\text{p-cymene})_2$ with P.P.



A mixture of  $\text{RhCl}_3(\text{p-cymene})_2$  (15 mg) and P.P. (20 mg) was heated under  $\text{H}_2$  gas in  $\text{CD}_6$  (0.6 g) at  $80^\circ\text{C}$  overnight. The NMR spectrum showed extensive H-incorporation in  $\text{CD}_6$  (5.9 % of  $\text{H}_3$ ) and the presence of two major species (-18 ppm, ( $\text{H}_2$ ) complex?) and -40 ppm.

## Reaction of $\text{RhHCl}(\text{PNCN})$ with $\text{H}_2\text{SiPh}$

A mixture of  $\text{RhHCl}(\text{PNCN})$  (6 mg) and  $\text{H}_2\text{SiPh}$  (30 mg) ~~in~~ in  $\text{CD}_6$  (0.6 g) was prepared. No reaction occurred at room temperature. The mixture was heated to  $60^\circ\text{C}$  for 10 minutes. There was evolution of  $\text{H}_2$ . The NMR spectrum showed broadened peaks (polymerization?).

The experiment was repeated using 2 mg  $\text{RhHCl}(\text{PNCN})$  and 30 mg  $\text{H}_2\text{SiPh}$ . The mixture was heated for 20 minutes at  $60^\circ\text{C}$  in  $\text{CD}_6$  (0.6 g).

Email from David Zengarian

- (1) mostly  $\text{Ph}_2\text{SiH}_2$  (5.2 ppm)
- (2)  $(\text{Ph}_2\text{SiH}_2)_2$  (4.5 ppm)
- (3) some oligomerization and possible cyclic oligomers

A mixture of  $\text{[IrCl}(\text{P-cymene})_2$  (15 mg), POP (20 mg) and  $\text{NET}_3$  (5 mg) in 2-propanoic acid (0.6 g) was heated at reflux for 12 hours. The NMR spectra showed the presence of several products.

### Reaction of $[\text{Ir}(\text{cod})\text{Cl}]_2$ with PNCNP

A mixture of  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (20 mg), PNCNP (25 mg) in 2-propanoic acid (0.6 g) was refluxed for 2 hours. The NMR spectrum showed the formation of one complex. (119 ppm (3H)).

### Preparation of $\text{IrHCl(PNCNP)}$

A mixture of  $[\text{IrCl}(\text{cod})]_2$  (200 mg) and PNCNP (250 mg) in 2-propanoic acid (2 ml) was refluxed for 2 hours under Argon. The mixture was cooled, the solids filtered, washed with 2-propanoic acid and  $\text{CH}_3\text{OH}$  and dried under vacuum.

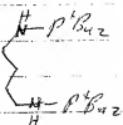
$$\text{yield} = 322 \text{ mg}$$

The NMR spectra showed a mixture of  $\text{IrHCl(PNCNP)}^{(62\%)}_{(62\%)}$  and  $\text{IrH}_2(\text{PNCNP})^{(38\%)}$

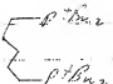
Reaction of Ir HCl(PNCN) with  $H_2SiPh$

A mixture of 225 mg of Ir HCl(PNCN) (from NMR reaction) and 85  $H_2SiPh$  (20%) was prepared in  $C_6D_6$  (0.6 g). The NMR spectrum showed the presence of 3 species.

Preparation of



Reaction of  $[Ir(cod)_2Cl_2$  with



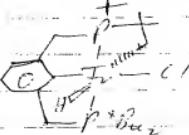
A mixture of  $[Ir(cod)_2Cl_2$  (20 mg) and the ligand (2.5 mg) in  $^2PbH$  (0.6 g) was refluxed for 30 minutes. TLC NMR spectrum showed the presence of  $[IrHCl(CP)]$  (2.0 mg) and  $[IrH_2(CP)]$ .

Reaction of  $[Ir(cod)_2Cl_2$  with



A mixture of  $[Ir(cod)_2Cl_2$  (10 mg) and  $PtC$  diphosphine (19 mg) was refluxed in 0.6 g  $^2PbH$  for 4 hours, during which a solid precipitated. The solid was filtered, washed with  $^2PbH$  and dried. It was dissolved in  $C_6D_6$  and the NMR obtained.

Product =  
based on NMR



Reaction of  $\text{Ir}(\text{cod})_2\text{Cl}_2$  with  $\text{P}^{\text{tBu}}_2$

A mixture of  $\text{Ir}(\text{cod})_2\text{Cl}_2$  (19 mg) and the diphosphine (20 mg) was prepared in Toluene (0.6 g). The NMR spectrum showed the presence of the  $\text{HCl}$  ( $\text{PCP}$ ),  $\text{IrH}_2$  ( $\text{PCP}$ ) and two other species after standing under  $\text{H}_2$  gas for 10 minutes.

The mixture was then degassed and left standing under Argon for 2 hours. The NMR spectrum showed the presence of the mono hydride, dihydride and a new species (-26.7 Hz -37.3 ppm (br)) in the hydride region.

A new sample was prepared and heated under  $\text{H}_2$  gas in Toluene ( $80^\circ\text{C}$ ) for 10 minutes. The NMR spectrum showed mainly the monohydride and dihydride complexes.

No significant change after heating for 2 hours.

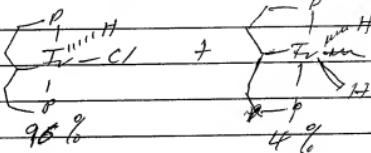
Reaction of  $\text{Ir}(\text{cod})_2\text{Cl}_2$  with  $\text{P}^{\text{tBu}}_2$

A mixture of  $\text{Ir}(\text{cod})_2\text{Cl}_2$  (20 mg) and the diphosphine (25 mg) in 2-pentanol (0.6 g) was refluxed under  $\text{H}_2$  gas for  $\frac{4}{4}$  hours. The NMR spectrum showed 82 % formation of the monohydride and 18 % of a new species.

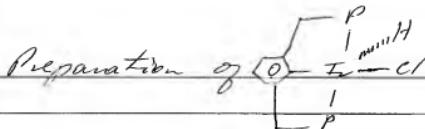
Reaction of  $\text{Ir}(\text{cod})_2\text{Cl}_2$  with  $\left\{ \begin{array}{c} \text{P}^{\text{Bu}_2} \\ \text{P}^{\text{Bu}_2} \end{array} \right.$

A mixture of  ~~$\text{Ir}(\text{cod})_2\text{Cl}_2$~~  ( $20\text{mg}$ ) and the ligand ( $25\text{mg}$ ) in 2-propano ( $0.6\text{g}$ ) was refluxed under  $\text{H}_2$  gas for 68 hours.

The sample was cooled to RT, decanted washed with 2-propano and distilled. The NMR spectrum in  $\text{CD}_3\text{O}_2$  showed the presence of:



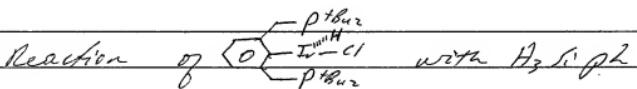
The experiment was repeated using  $\text{Ir}(\text{cod})\text{Cl}_2$  ( $20\text{mg}$ ) and ligand ( $22\text{mg}$ ) and refluxing in 2-pentanol for 3 days. It was cooled, decanted, washed with 2-propano and dried. The NMR spectrum showed the monohydride ( $90.5\%$ ), ~~and~~ 2 other dihydrides ( $1.81\%$ ) and 2 other species ( $7.89\%$ ) and ( $3.80\%$ ).



A mixture of  $\text{Ti}(\text{OC}_2\text{CH}_3)_4$  (200 mg) ~~and~~ and the diphenylphosphine (250 mg) in 2-pentanol (5 g) was refluxed under  $\text{H}_2$  gas for 4 hours. The solids were filtered, washed with 2-propanol and dried under vacuum. The NMR spectrum showed the presence of the mono-hydride complex 62% and a dihydride species (18%). They were separated by ~~distillation~~ repeatedly decanting <sup>(contains tetrahydro)</sup> the ~~upper~~ supernatant portions <sup>(contains tetrahydro)</sup> of the mixture in 2-pentanol.

$$\text{Yield of monohydride} = 220 \text{ mg}$$

$$\text{Yield of dihydride} = 116 \text{ mg.}$$



A mixture of the monohydride compound (200 mg) and  $\text{H}_2\text{SiPh}_2$  (80 mg) in  $\text{C}_6\text{D}_6$  (0.6 g) was left standing overnight. The NMR spectrum showed the formation of a species in 83% ( $^{29}\text{P}$ ) along with 4 minor species (2.6, 8.1, 8.8 and 5.4%).

Reaction of  $\text{Ir}(\text{CO})_2\text{Cl}_2$  with  $\left\{ \begin{matrix} \text{PPh}_3 \\ \text{NH} \end{matrix} \right.$

A mixture of  $\text{Ir}(\text{CO})_2\text{Cl}_2$  (20 mg) and the ligand (25 mg) was refluxed for ~~30 minutes~~ in 2-AcH (0.6 g). A precipitate resulted. The supernatant was decanted, the solids washed with 2-pyOH and dried under vacuum. The NMR spectrum in  $\text{CD}_2\text{Cl}_2$  showed the presence of 3 complexes ( $\delta\text{H}$  - 84.1%, 8%, 8%).

The above reaction was repeated using toluene and ~~refluxing at 80°C~~ for 20 minutes. The NMR spectrum showed the presence of 6 complexes ( $\delta\text{H}$ , 1.8%, 1.8%, 20.4%, 68.4%, 6.5%, 1.2%).

A mixture of  $\text{Ir}(\text{CO})_2\text{Cl}_2$  (22 mg) and the diphosphine (15 mg) was prepared in toluene. (Room Temp). The NMR spectrum showed the formation of one main species (95%). Broad hydride signal (~ 25.4 ppm).

A mixture of  $(\text{Ir}(\text{cod})_2(\text{PPh}_3)^{\text{(bromide)}}$  and the PNHP ligand (20 mg) was refluxed in  $\text{C}_6\text{D}_6$  (0.6 g) for 8 hours. A colourless solid precipitated. The supernatant was decanted and the solid dissolved in  $\text{CH}_2\text{Cl}_2$ . The NMR spectrum showed the formation of one product as a mixture of 150 to 200 mers.

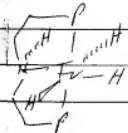
### Preparation of $\text{FrHCl}(\text{PNHP})(\text{cod})$ .

A mixture of  $(\text{Ir}(\text{cod})_2(\text{PPh}_3)$  (60.675 g) and the diphosphine PNHP (0.540 g) was dissolved in 0.5 ml toluene and stirred for 20 minutes. A colourless ppt started to form and hexanes (10 ml) was added. The mixture was stirred for an additional 30 minutes. The solids were filtered, washed with hexanes, and dried under vacuum.

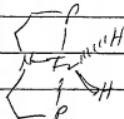
$$\text{yield} = 0.772 \text{ g.}$$

### Preparation of $\text{FrH}_3(\text{PNHP})$

A mixture of  $\text{FrHCl}(\text{PNHP})(\text{cod})$  (100 mg) and  $\text{NaBH}_4$  (30 mg) in  $\text{EtOH}$  (2 ml) was warmed at  $60^\circ\text{C}$  for 20 minutes. The colourless solids were filtered, washed with  $\text{EtOH}$  and dried under vacuum. The NMR spectrum in  $\text{CD}_2\text{Cl}_2$  (insoluble in  $\text{C}_6\text{D}_6$ ) showed the presence of  $\text{FrH}_3(\text{PNHP})$ . Note - NaI was not removed.



## Preparation of IrH<sub>2</sub>(PPh<sub>3</sub>)



A mixture of IrH<sub>2</sub>(PNHD) (30 mg) in C<sub>6</sub>D<sub>6</sub> (0.6 g) was refluxed under Argon, with degassing and refilling with Ar (3 times). The colourless solution changes to yellow. The NMR spectrum showed the clean formation of IrH<sub>2</sub>(PPh<sub>3</sub>).

A mixture of Ir(CO)<sub>2</sub>Cl<sub>3</sub> (30 mg) was refluxed (80°) in toluene for 8 hours. The NMR spectrum showed the formation of only one complex as a mixture of isotopomers. Integrate for 1 hydride (?).

300 mg of Acetophenone; 10 mg of IrH<sub>2</sub>(PNHD) and 2.5 g of 2-propanethiol was refluxed for 6 hours at 80°C. The NMR spectrum showed the formation of phenyl ethanol (80% !!).

The above ~~by~~ transfer by hydrogenation was repeated. The NMR showed 86% conversion of the ketone to the alcohol.

A mixture of 50 mg of acetophenone, 2.5 g 2-propanone and 70 mg of IrH<sub>2</sub>(PNHP) was refluxed (2 hours) in an open test tube (IN AIR). The NMR spectrum showed 98% conversion of the ketone to the alcohol.

### Preparation of Ir HCl(PNP)(OEt)

The complex was prepared using 2.09 g [Ir(OEt)<sub>2</sub>]Cl<sub>2</sub> (2.09) and PNHP (1.65 g). Yield = 2.32 g.

### Preparation of IrH<sub>2</sub>(OVO)

150 mg of IrH<sub>2</sub>(PNHP) was sublimed under dynamic vacuum for 2 hours at 150°C. Yield = 132 mg of the dihydride.

~~Ethanol~~ Ethanol (5 ml) was added to a mixture of Ir HCl(PNP)(OEt) (1.2g) and NaBH<sub>4</sub> (100mg) and the mixture warmed for 20 minutes at 60°C. The solids were filtered, washed with ethanol and dried under vacuum. They were repeatedly extracted with 4 x 5 ml of CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts was evaporated to dryness, under vacuum (refluxing with H<sub>2</sub> if solution becomes yellow). Ethanol (2 ml was then added) and

The mixture stirred for 20 minutes under ~~the~~ nitrogen. The solids were filtered and dried under vacuum. Yield = 0.682g.

### Hydrogenation of cyclohexanone [3]

A mixture of cyclohexanone (200 mg), 2-propanethiol (2.5g) and  $TiH_3(PNHD)$  (3mg) was refluxed for 4 hours. The NMR spectrum showed 100 % conversion of the ketone to the alcohol.

### Hydrogenation of 2-pentanone [4]

A mixture of 200 mg of the ketone, 2.5g 2-propanethiol and 5mg of  $TiH_3(PNHD)$  was refluxed for 4 hours under ~~the~~ Argon. The NMR spectrum showed 100 % conversion to the alcohol.

### Hydrogenation of Benzophenone [5] [6]

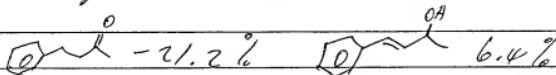
200 mg ketone, 2.5g 2-propanethiol, 5mg  $TiH_3(PNHD)$  reflux for 4 hours. 27% formation of the alcohol.

Hydrogenation of benzalacetone

200 mg acetone, 2.5 g 2-propanoic acid, 5 mg IrH<sub>2</sub>(ONHO)

reflux for 4 hours.

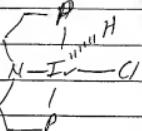
NMR spectrum showed 27.6 % conversion



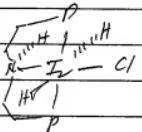
A mixture of IrH<sub>2</sub>(ONHO) (75 mg) and 2-propanoic acid (10 mg) was prepared in 2-propanol (10 mL). The NMR spectrum showed no formation of ~~IrH<sub>2</sub>(ONHO)~~.

The mixture was heated for 2 hours at 80°C. No formation of IrH<sub>2</sub>(ONHO) was observed.

A mixture of IrHCl(ONP)6Oe (25 mg) and 2-propanoic acid (10 mg) in C<sub>6</sub>D<sub>6</sub> (0.6 g) was heated at 80°C for 40 minutes. ~~Red~~ colourless oil formed. The solvent was decanted, dried and the solids dissolved in C<sub>6</sub>D<sub>6</sub>. The NMR spectrum showed one compound as a mixture of 130% powers.



A mixture of  $\text{IrHCl}(\text{PNO})(\text{OEt})$  (250 mg), 2-propanol (200 mg) in hexane (2 g) was refluxed for 1 hour, yielding a dark red solid. This was washed with hexanes and dried under vacuum. Yield = 192 mg.



### Preparation of $\text{IrH}_2(\text{PNHP})$ .

A solution of  $\text{IrHCl}(\text{PNO})(\text{OEt})$  (10 mg) in  $\text{CH}_2\text{Cl}_2$  (0.8 g) was exposed to an atmosphere of  $\text{H}_2$  gas. The NMR spectrum showed the formation of trans-  $\text{IrH}_2(\text{PNHP})$ .

### Hydrogenation of Acetophenone:

1.09 g Acetophenone, 3.09 g 2-propanol, 10 mg of  $\text{KOMe}$  and 10 mg of  $\text{IrH}_2(\text{PNHP})$  was refluxed at  $80^\circ\text{C}$  for one hr. The NMR spectrum showed 82 % conversion of the ketone to the alcohol.

### Preparation of $\text{EH}(\text{OEt})_2\text{Zr}(\text{BAAF})_2$ :

715 mg of  $\text{Zr}(\text{BAAF})_2$  and 1000 mg of 2M HCl solution in  $\text{Et}_2\text{O}$  and 1.5 ml of ether was stirred for 30 minutes. The optil NaCl was removed by filtration and 15 ml of hexane added. Stirring with a spatula resulted in colourless crystals of the product. Yield = 715 mg.

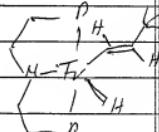
Reaction of  $\text{InH}_2(\text{PNP})$  with  $\text{H}_3\text{SiOH}$ .

30 mg of the dihydride and 6 mg of  $\text{H}_3\text{SiOH}$  in  $\text{CsD}_6$  (0.6 g) showed the clear formation of the 11-silane trihydride complex.

Reaction of  $\text{InH}_2(\text{PNP})$  with  $\text{H}_3\text{SiOH}$ .  
 A mixture of the trihydride complex (50 mg) and  $\text{H}_3\text{SiOH}$  (3 mg) in  $\text{CsD}_6$  (0.6 g) showed the formation of 14 % of the 6-silane complex.  
 47 % after 4 days  
 80 % after 1 week

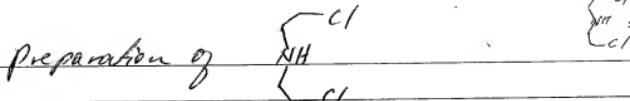
Reaction of  $\text{InH}_2(\text{PNP})$  with  $\text{H}-\text{C}\equiv\text{C}-$

A mixture of  $\text{InH}_2(\text{PNP})$  (20 mg) and 15 alkyne (30 mg) was left standing for two days. The NMR spectrum showed the formation of vinyl complex.

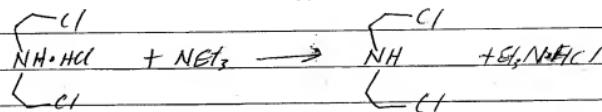


Preparation of

2.8

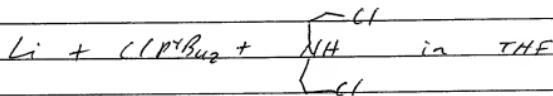


$$\begin{cases} \text{mass} \\ \text{C1} \\ \text{C1} \end{cases} = 0.67g$$



1.59 g of bis(chloroethyl)amine hydrochloride was warmed at 50°C for 24 hours in NET<sub>3</sub> (5 ml) with stirring. The mixture was filtered, the solids washed with 5 ml of NET<sub>3</sub>, and the combined filtrate evaporated under vacuum. The remaining pale yellow liquid was distilled under vacuum at 50°C, yielding bis(chloroethyl)amine as a colourless liquid.

$$\text{Yield} = 0.67g.$$

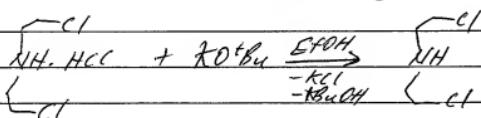


Lithium metal (0.459) was added to a mixture of CIPBu<sub>2</sub> (2.74 g) and bis(chloroethyl)amine (3.7 g) in THF (15 g) at -80°C. The mixture was stirred for 1 hour, then allowed to reach room temp (1 hour). The mixture was then stirred for an additional 4 hours at room temperature. The mixture showed a major peak at -21.2 ppm (<sup>31</sup>PF<sup>1</sup>H).

Preparation of  $\text{LiP}^+\text{Bu}_2$ .



$\text{CIPtBu}_2$  (14 g) was added in 7 ml portions to a vigorously stirred mixture of THF (140 ml) and lithium granules (1.5 g). The additional portions of  $\text{CIPtBu}_2$  were added only after the reaction mixture developed a distinct yellow colour (5-10 min) (caution!! faster addition results in boiling and the mixture being thrown out of the flask). After addition was complete, the mixture was stirred at room temperature for 72 hours. The NMR spectrum showed 96%  $\text{LiP}^+\text{Bu}_2$ .



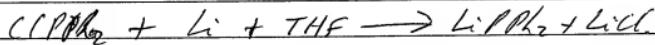
A mixture of bis(chloroethyl)amine hydrochloride (17.8 g) and  $\text{KO}^+\text{Bu}$  (11.5 g) in EtOH (50 ml) was stirred at room temperature for 4 hours. The mixture was filtered and evaporated under reduced pressure.

yield of crude bis(chloroethyl)amine = 12.92 g  
The crude amine was distilled at  $50^\circ\text{C}$  under vacuum yielding 11.52 g of pure bis(chloroethyl)amine.

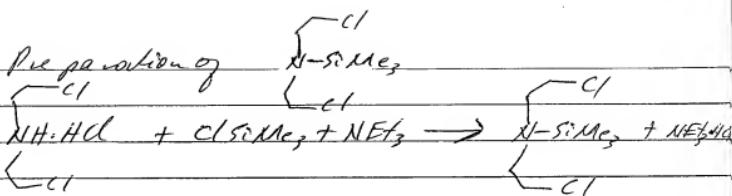


16 g of bis(chloroethyl)amine was added to the solution of  $\text{LiPPh}_2$  in THF (from 04/02/03) at  $-80^\circ\text{C}$ . The mixture was stirred at  $-80^\circ\text{C}$  for 1 hour and allowed to reach room temperature slowly ( $\approx 2$  hours). The mixture was then stirred for an additional 4 hours at room temperature, then refluxed (1 hour). It was then filtered, the THF removed under reduced pressure and the phosphine distilled. The fraction which boiled at  $60^\circ\text{C}$  under vacuum was collected. The NMR spectrum showed the aginolite (93%).

  $\text{P}^+\text{Ph}_2$  yield = 8.2 g.

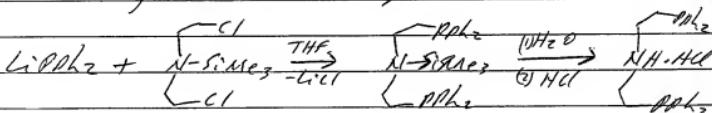


$\text{CIPPh}_2$  (15.0g) was added in 2 ml portions to a stirred suspension of Li granules (1.5g) in THF (50 ml). Caution!!! The resulting mixture was stirred for 72 hours at room temperature. The NMR spectrum showed 97%  $\text{LiPPh}_2$ .

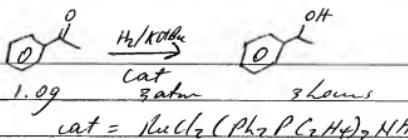


A mixture of bis(chloroethyl) amine hydrochloride (75g); Et<sub>3</sub>N (600 ml) and C<sub>2</sub>H<sub>5</sub>SiMe<sub>3</sub> (400ml) was heated to reflux for 12 hours. The mixture was cooled and filtered. The ~~solid~~ solid was washed with 50ml Et<sub>3</sub>N and the combined filtrate evaporated to give a yellow oil. This was diluted with benzene (25 ml) and the resulting mixture filtered. The solution was evaporated under vacuum to yield the product. It was stored in the refrigerator of the glove box.

yield = 26.82g.

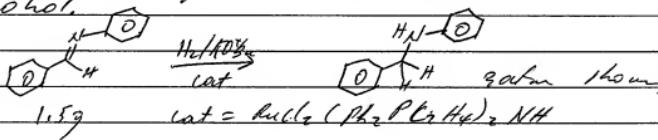


A solution of  $(\text{C}(\text{CH}_2\text{CH}_2)_2\text{NSiMe}_3$ ) (8.5g) in THF (10ml) was added to the mixture of LiOPh<sub>2</sub> (from 1162/03) at -40°C. The mixture was allowed to warm to room temp, stirred for 1 hour then refluxed for 1 hour. The white suspension was then cooled to R.T. and 15 ml of water added. It was stirred for 1 hour at room temp, the bottom (water)

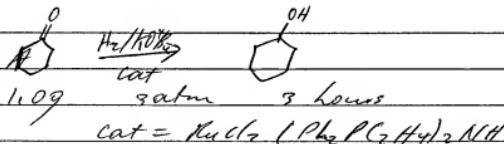


A mixture of acetophenone (1.0g),  $\text{KOtBu}$  (10mg) and catalyst (10mg) was stirred under  $\text{H}_2$  gas (3 atm) for 3 hours.

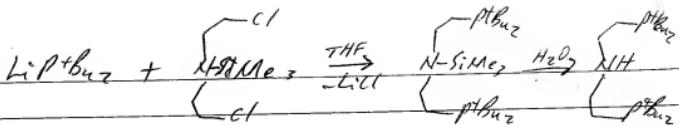
The NMR spectrum showed 100 % conversion of the ketone to the alcohol.



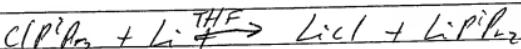
A mixture of the imine (1.5g),  $\text{KOtBu}$  (10mg) catalyst (10mg) was stirred under  $\text{H}_2$  gas (3 atm) for 1 hour. The NMR spectrum showed 100 % conversion of the imine to the amine.



A mixture of the ketone (1.0g),  $\text{KOtBu}$  (10mg) and catalyst (10mg) in 2-propanol was stirred under  $\text{H}_2$  gas (3 atm) for 3 hours. 100 % conversion to the alcohol.

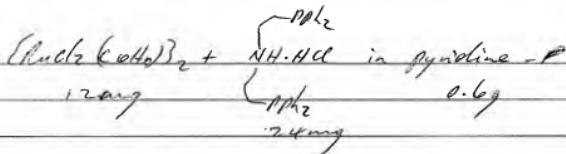


A solution of  $(\text{C}(\text{CH}_2\text{CH}_3)\text{NSiMe}_3$  (9.0g) in THF (10ml) was added slowly to a solution of  $\text{LiP}^{\ddagger}\text{Bu}_2$  in THF (from 17/02/03) at  $-80^\circ\text{C}$ . The mixture was then allowed to warm to room temperature and stirred for 1 hour. It was then refluxed for 1 hour. 15 ml of water was added after the mixture cooled to R.T. and stirred for 1 hour. The aqueous layer was removed and another 15 ml of  $\text{H}_2\text{O}$  added. The mixture was refluxed for 14 hours (with 20ml of benzene). The aqueous layer was removed and the mixture evaporated to dryness. It was then distilled under vacuum. The fraction boiling between  $150-160^\circ\text{C}$  was collected. Yield = 17.22g.



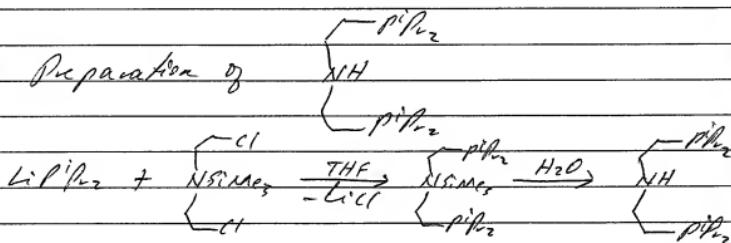
11.0g 1.5g

$\text{CIP}^{\ddagger}\text{Bu}_2$  (11.0g) was added in 2g portions to a suspension of Li granules (1.5g) in THF (40ml) (Caution!!) The mixture was stirred for 3 days at room temperature.



Pyridine (0.6 g) was added to a mixture of  $\text{RuCl}_2(\text{C}_6\text{H}_5)_2$  and  $\text{Ph}_3\text{P}(\text{C}_2\text{H}_5)_2\text{NH}_3\text{HCl}$  (24 mg).

Preparation of  $\begin{cases} \text{Cl} \\ \text{N-SiMe}_3 \end{cases}$  - as per procedure.



A solution of  $(\text{C}_2\text{H}_5)_2\text{N-SiMe}_3$  (7.75 g) in 10 ml THF was added to a solution of  $\text{LiPiPr}_2$  (from 24/02/03) at  $-80^\circ\text{C}$ . The mixture was then allowed to warm to room temperature and refluxed for 1 hour. 15 ml of water was added and the mixture was stirred at R.T. for 1 hour. The aqueous layer was removed and 15 ml of water and 15 ml of hexanes added. The mixture was refluxed for 4 hours and the aqueous layer removed after cooling. The mixture was evaporated to dryness and distilled under vacuum. The fraction

36

Preparation of  $\text{Li}^+\text{Ph}_2$  - As per procedure

Preparation of  $\text{NH}$   $\begin{cases} \text{Ph}_2 \\ \text{Ph}_2\text{H}_2 \end{cases}$  As per procedure  
 $\text{Ph}_2\text{H}_2$  - Double distilled.

yield = 12.56 g from 15g  $\text{ClPh}_2$

$\begin{cases} \text{Ph}_2 \\ \text{Ph}_2 \end{cases}$   $\text{NH}, \text{HCl}$  +  $\text{Ir}(\text{cod})_2(\text{Bz})_2 + \text{NET}_3$  in  $\text{C}_6\text{D}_6$   
 $\begin{cases} \text{Ph}_2 \\ \text{Ph}_2 \end{cases}$  15mg 12mg 30mg 0.6g

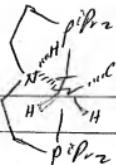
Heat for  $80^\circ\text{C}$  for 10 minutes. Only 1 product formed (NMR).

Reaction of  $\text{NH}$  with  $\text{Ir}(\text{cod})_2(\text{Bz})_2$   
~~Ph<sub>2</sub>H<sub>2</sub>~~  $\begin{cases} \text{Ph}_2 \\ \text{Ph}_2 \end{cases}$   
0.6g 10mg " mg

iPrOH R.T. - 1 product after 5 mins, 10 mins, 1hr.  
 $80^\circ\text{C}$  for 10 minutes - main prod. = 89%

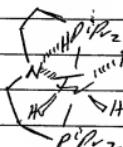
$\text{C}_6\text{D}_6$  R.T. - several products - 10 minutes.  
 $80^\circ\text{C}$  for 4 hours - several products

Preparation of



2-propanol (3 ml) was added to a mixture of  $(\text{Ir}(\text{C}_5\text{H}_5)\text{Cl}(\text{P}_2\text{C}_2\text{H}_4))_2$  (1.5 g) and  $(\text{iPr}_2\text{P}(\text{C}_2\text{H}_4))_2\text{NH}$  (1.02 g) and the mixture warmed for 45 minutes at  $80^\circ\text{C}$ . ~~The~~ Hexanes (6 ml) were then added and the white precipitate filtered, washed with hexanes and dried under vacuum. Yield = 105.2 g.

Preparation of

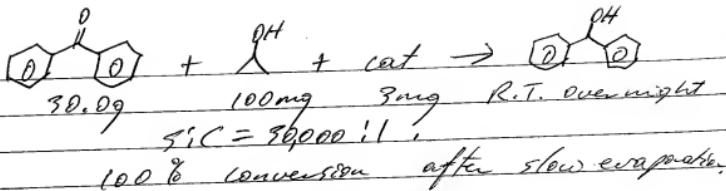


$(\text{IrH}_2\text{Cl}((\text{iPr}_2\text{P}(\text{C}_2\text{H}_4))\text{NH})) + \text{superhydride in THF}$   
 20 mg 3.0 mg 1.0 M  $\text{NaBH}_4$  0.69  
 1 hour at R.T.

The NMR spectrum showed the formation of  $(\text{IrH}_3((\text{iPr}_2\text{P}(\text{C}_2\text{H}_4))\text{NH}))$  as the only product.

A mixture of  $\text{IrH}_2\text{Cl}(\text{PNaO})$  (800 mg) and superhydride (1600 mg, a 1M  $\text{NaBH}_4$  in THF) in THF (2 ml) was stirred for 12 hours at R.T. The mixture was evaporated to dryness and extracted with  $3 \times 10$  ml toluene. The filtrate was evaporated to dryness, yielding the product as a viscous oil, which solidifies after 10 days. Yield = 62%.

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### KINETIC STUDY

using  $\text{IrH}_2(\text{PPh}_3)_2\text{Cl}$

Preparation of catalyst solution:

(1) 0.15 mg of catalyst was dissolved in 10 ml iPrOH.  
 (2) 0.7 ml of the solution was diluted to 10 ml in iPrOH.  
 (3) 0.059 g of Re solution was mixed with 0.109 g Acetophenone and the mixture quickly equilibrated at the required temperature and the reaction monitored by  $^1\text{H NMR}$ .

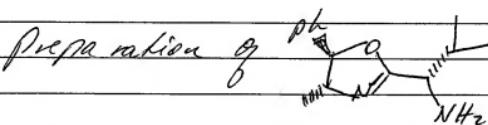
Final Substrate: Catalyst ratio = 7200:1

Time/min	25 °C		40 °C		50 °C			
	[O] <sup>L</sup>	[O] <sup>SH</sup>	[O] <sup>L</sup>	[O] <sup>SH</sup>	[O] <sup>L</sup>	[O] <sup>SH</sup>		
5	91.06	8.94	5	71.25	28.75	2	87.79	12.21
10	86.96	13.04	10	59.09	40.91	4	80.90	19.10
15	83.47	16.53	15	51.67	48.33	6	73.65	26.35
20	81.32	18.68	20	43.71	56.29	8	68.02	31.98
30	76.77	23.23	30	37.85	67.15	10	62.52	37.48
40	72.26	27.74	40	26.01	73.99	12	58.99	41.01
60	64.89	35.11	50	22.11	77.89	16	51.41	48.59
100	50.79	49.21				20	44.38	55.62
						40	28.02	71.98
							34.35	65.45

## Kinetic study

Contd

55 °C				60 °C				70 °C			
Time min	(O) <sup>I</sup>	(O) <sup>II</sup>									
2.5	88.13	31.87	2.5	68.66	31.35	2.5	80.16	19.84			
4	59.65	40.35	4	34.92	45.08	4	62.12	37.83			
6	50.67	49.33	6	45.29	54.71	6	36.09	43.91			
8	40.01	59.99	8	38.30	61.70	8	51.43	48.57			
10	33.33	66.67	10	32.80	67.20	10	46.21	53.79			
12	29.22	70.78	12	29.17	70.83	12	42.14	57.86			
16	23.23	76.77	16	23.77	76.23	16	31.88	68.12			
20	21.65	78.35	20	21.11	78.89	18	29.13	70.87			
30	19.41	80.59				22	25.23	74.77			



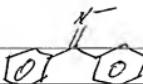
Ocam

The oxazoline amine was prepared as illustrated in the literature by Sigman et al. - Organic Letters, 2002. The ligand was used for the preparation of ruthenium complexes without further purification.

Preparation of RuHCl(CpH<sub>3</sub>)<sub>2</sub>(Ocam)

Toluene (5 mL) was added to a mixture of RuHCl(CpH<sub>3</sub>)<sub>2</sub> (30 mg) and enough Ocam to change the colour to a green solution. This solution was used for reactions.

Preparation of



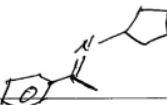
A mixture of benzophenone (3 g) and 2M methylamine solution in THF (100 ml) was refluxed over activated molecular sieves for 24 hours in a pressure flask. The mixture was then refluxed for an additional 48 hours after an additional 100 ml of the methylamine solution was added. The solvent and excess reagent was removed under vacuum. Yield = 4.8 g.

Preparation of



A mixture of benzaldehyde (10 g) and 2M ethylamine solution in THF 200 ml was stirred over activated molecular sieves for 12 hours. The mixture was ~~filtered~~ filtered and the solvent and excess reagents removed under vacuum. Yield = 8.2 g.

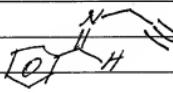
Preparation of



A mixture of acetophenone (10g) and cyclopentylamine (15g) ~~in~~ toluene (30 ml) was refluxed for 48 hours over activated molecular sieves.

The mixture was filtered, and the solvent and excess reagents removed under vacuum. The product was purified by distillation under vacuum.  
Yield = 7.2 g.

Preparation of



A mixture of benzaldehyde (10g) and propargyl amine (10g) in THF (50 ml) was stirred over activated molecular sieves for 12 hours.

The solvent was removed and the excess reagents were removed under vacuum. Yield = 7.0 g.

Preparation of



A mixture of acetophenone (5 g) and propargylamine (10 g) in toluene (25 ml) was refluxed for 48 hours over activated molecular sieves.

The solvents and excess reagents were removed under vacuum.

Yield = 3.7 g.

Preparation of RuHCl(*pph*<sub>3</sub>)<sub>3</sub>

Toluene (100 ml) was added to RuCl<sub>2</sub>(*pph*<sub>3</sub>)<sub>3</sub> (6 g), followed by *NEt*<sub>3</sub> (2 g). The mixture was flushed with argon gas, then flushed with hydrogen gas on a Schlenk line and refluxed for 12 hours under hydrogen gas. The mixture was allowed to cool to room temperature and stirred overnight. It was then filtered, washed with ethanol (3 x 20 ml) then ether and dried under vacuum. Yield = 4.72 g.

## Preparation of RuHCl(Binap)(PPh<sub>3</sub>)

THF (20 ml) was added to a mixture of RuHCl(PPh<sub>3</sub>)<sub>3</sub> (1.5 g) and R-binap (1.1 g). The mixture was refluxed for 12 hours under argon. The solvent was then removed under vacuum. The solids were extracted with 3 x 20 ml of dichloroethane and the combined filtrate was concentrated to 3 ml. Hexanes (25 ml) was added to precipitate the red-orange product.

$$\text{yield} = 1.39 \text{ g.}$$

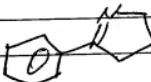
## Preparation of R,R'-Appach

A solution of chlorodiphenylphosphine (3.83 g) dissolved in toluene (20 ml) was added dropwise to a solution of K,R'-cyclohexyl/diamine (1.09) and Triethylamine (1.8 g) in toluene (20 ml). The mixture was then stirred for 6 hours under argon. It was then filtered, the solids washed with toluene, and the combined filtrate concentrated to 3 ml by evaporation under vacuum. Hexanes (30 ml) was then added, precipitating a white solid. This was filtered, washed with hexanes and dried under vacuum. Yield = 4.03 g.

Preparation of  $\text{RuHCl}(\text{dppach})(\text{pph}_3)$

THF (10 ml) was added to a mixture of  $\text{RuHCl}(\text{pph}_3)$  (1.5 g) and dppach (0.83 g) and the resulting mixture was refluxed for 17 hours under argon. The mixture was filtered and concentrated to 3 ml under vacuum. 20 ml of hexanes was then added and the mixture stirred for 4 hours under argon. A brick red product precipitated. This was collected, washed with hexanes and dried under vacuum. Yield = 1.29 g.

Preparation of



This was prepared using the procedure outlined by Sogi et al. JACS 1990, 112, 3567-79 and Kirsch et al. Tet. Lett. 2001, 42, 6101-04.

Kirsch method better, 92% yield !!

[REDACTED] Preparation of



This was prepared as outlined in  
Ballal et al. Org. prep. proc. Int. 1987, 21, 283.

[REDACTED] Preparation of RuHCl(R-binap)(R,R-cydi)

THF (2 ml) was added to a mixture  
of RuHCl(R-binap)( $\text{PPh}_3$ ) (300 mg) and  
D.R,R-cydi (40 mg) and the solution  
stirred for 1 hour under argon. The  
mixture was filtered and hexanes  
(15 ml) added, precipitating a bright  
yellow solid. Yield = 235 mg.

[REDACTED] Preparation of RuHCl(R-binap)(RR-cydi)

300 mg of RuHCl(R-binap)( $\text{PPh}_3$ ) and  
60 mg of R.R-cydi were dissolved  
in 1 ml of THF and the mixture  
stirred for 30 minutes. The solution  
was filtered and hexanes (10 ml)  
added to the filtrate, precipitating  
a yellow solid. Yield = 261 mg.

Preparation of RuHCl(R,R-dppach)(C<sub>20</sub>H<sub>32</sub>)

THF (2ml) was added to a mixture of 300 mg RuHCl(R,R-dppach)(C<sub>20</sub>H<sub>32</sub>) and 35 mg of R,R-cyclon. The mixture was stirred for 1 hour under argon. It was filtered and 10 ml of hexanes added, precipitating a yellow-green solid. yield = 236 mg.

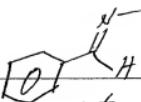
Preparation of RuHCl(R,R-dppach)(C<sub>20</sub>H<sub>32</sub>)

300 mg of RuHCl(R,R-dppach)(C<sub>20</sub>H<sub>32</sub>) and 66 mg R,R-dpen were added to 1ml of THF and the mixture stirred for 30 minutes. The mixture was filtered and hexanes (10ml) was added, precipitating an orange-red solid. yield = 274 mg.

Preparation of RuCl(R,R-dppach)(C<sub>20</sub>H<sub>32</sub>)

Toluene (5ml) was added to a mixture of RuHCl(R,R-dppach)(C<sub>20</sub>H<sub>32</sub>) (600 mg) and enough oxone to change the colour to a bright yellow-green. This solution was used as a catalyst stock solution.

**[REDACTED]** Hydrogenation of



Cat = RuHCl(R-bings)(R<sub>2</sub>B<sub>9</sub>)

0.68 g of the imine was dissolved in deuterated benzene (2 ml) and added to a 50 ml Parr reactor containing RuHCl (R-bings) (R<sub>2</sub>B<sub>9</sub>-cyclic) (5 mg) and KOBu (10 mg) under Hydrogen gas. The reactor was pressurized to 15 bar and stirred for 24 hours at room temperature. The NMR spectrum of the reaction mixture showed complete conversion to the amine.

**[REDACTED]** Cat = RuHCl(R-bings)(R<sub>2</sub>R-open).

H<sub>2</sub> = 15 bar, Imine = 0.61 g, Cat = 5 mg, KOBu = 10 mg.  
The reaction was setup as above  
NMR showed 100% conversion after 24 hours.

**[REDACTED]** Cat = RuHCl(R<sub>2</sub>R-approach)(R<sub>2</sub>B<sub>9</sub>-cyclic)

H<sub>2</sub> = 15 bar, Imine = 0.81 g, Cat = 5 mg, KOBu = 10 mg.  
As above. Yield = 100% amine (NMR).

**[REDACTED]** Cat = RuHCl(R<sub>2</sub>R-approach)(R<sub>2</sub>R-open)

Imine = 0.71 g, Cat = 5 mg, KOBu = 10 mg

H<sub>2</sub> = 15 bar. As above

NMR showed 100% conversion to amine.

## Hydrogenation of

A mixture of the imine (0.56g) in  $\text{CH}_2\text{Cl}_2$  (2 ml), catalyst ( $\text{RuHCl}(\text{R}-\text{binap})(\text{R},\text{R}-\text{cyd})$ , 5 mg) and  $\text{KO}^+\text{Bu}$  (10 mg) ~~10 mg~~ in a gas pressure reactor was stirred under hydrogen (30 bar) for 24 hours. The NMR of the reaction mixture showed complete conversion of the imine to the amine.

Cat =  $\text{RuHCl}(\text{R}-\text{binap})(\text{R},\text{R}-\text{open})$

Cat = 5 mg, imine = 0.50 g,  $\text{KO}^+\text{Bu}$  = 10 mg  
 $\text{H}_2$  = 30 bar. Reaction as above.

NMR showed complete conversion of the imine to amine.

Cat =  $\text{RuHCl}(\text{R},\text{R}-\text{dppach})(\text{R},\text{R}-\text{cyd})$

Cat = 5 mg, imine = 0.67 g,  $\text{KO}^+\text{Bu}$  = 10 mg  
 $\text{H}_2$  = 30 bar.

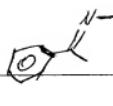
NMR = 100% conversion.

Cat =  $\text{RuHCl}(\text{R},\text{R}-\text{dppach})(\text{R},\text{R}-\text{dpn})$

Cat = 5 mg, imine = 0.59 g,  $\text{KO}^+\text{Bu}$  = 10 mg  
 $\text{H}_2$  = 30 bar.

NMR showed 100% conversion.

Hydrogenation of



Cat = RuHCl(R-binap)(R,R-cyclon)

A mixture of the imine (0.45 g), catalyst (5 mg) and KOTBu (10 mg) ~~was~~ in C6D6 (2 ml) was stirred under H<sub>2</sub> gas (30 bar) for 24 hours at room temperature. The NMR spectrum showed 98% conversion of the imine.  
 $\Delta\delta$  (c=2, chloroform) = -44.6°

Cat = RuHCl(R-binap)(R,R-cyclon)

Cat = 5 mg, Imine = 0.441 g, KOTBu = 10 mg,  
 H<sub>2</sub> = 30 bar.

NMR showed ~~97%~~ 97% conversion.

$$\Delta\delta = -51.1^\circ.$$

Cat = RuHCl(R,R-cyclon) (R,R-cyclon)

Cat = 5 mg, Imine = 0.54 g, KOTBu = 10 mg,  
 H<sub>2</sub> = 30 bar.

NMR showed 100% conversion of the imine to amine.

$$\Delta\delta = -34.6^\circ.$$

Cat = RuHCl(R,R-cyclon) (R,R-cyclon)

Cat = 5 mg, Imine = 0.48 g, KOTBu = 10 mg,  
 H<sub>2</sub> = 30 bar.

100% conversion to amine.

$$\Delta\delta = -36.7^\circ.$$

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## Hydrogenation of [O]<sup>N</sup>

Cat = RuHCl(R-binap)(RR'-cydru), H<sub>2</sub> = 30 bar  
A mixture of the catalyst (5mg), KOTBu (10 mg), Iminine (0.429) in C<sub>6</sub>D<sub>6</sub> (2 ml) was stirred for 36 hours at room temperature. The NMR spectrum showed 95% conversion.

Cat = RuHCl(RR-binap)(RR'-dopen)

Cat = 5mg, Iminine = 0.389, KOTBu = 10mg  
H<sub>2</sub> = 30 bar.

NMR showed 98% conversion.

Cat = RuHCl(RR-dppach)(R,R'-cydru)

Cat = 5mg, Iminine = 0.59, KOTBu = 10mg,  
H<sub>2</sub> = 30 bar.

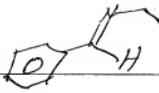
100 % conversion after 24 hours

Cat = RuHCl(R,R-dppach)(R,R'-dopen)

Cat = 5mg, Iminine = 0.449, KOTBu = 10mg  
H<sub>2</sub> = 30 bar.

NMR showed complete conversion  
after 24 hours.

Hydrogenation of



Catalyst = RuHCl(R-binap)(R,R-cycl).

A mixture of the catalyst (5 mg),  $\text{KO}^+\text{Bu}$  (10 mg), Tinine (0.45 g) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was stirred under hydrogen gas (15 bar) for 24 hours.

The NMR showed 100 % conv.

Cat = RuHCl(R-binap)(R,R-cycl).

Cat = 5 mg, Tinine = 0.41 g,  $\text{KO}^+\text{Bu}$  = 10 mg  
 $\text{H}_2$  = 15 bar.

Complete conversion in 24 hours.

Cat = RuHCl(R, R-dppach)(R,R-cycl)

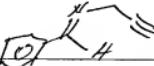
Cat = 5 mg, Tinine = 0.54 g,  $\text{KO}^+\text{Bu}$  = 10 mg  
 $\text{H}_2$  = 15 bar.

100 % conversion in 24 hours.

Cat = RuHCl(R,R-dppach)(R,R-cycl)

Cat = 5 mg, Tinine = 0.48 g,  $\text{KO}^+\text{Bu}$  = 10 mg  
 $\text{H}_2$  = 15 bar.

Complete conversion in 24 hours.

Hydrogenation of 

Cat = RuHCl(R-binap)(R,R-*cycl*)

A mixture of the catalyst (3mg),  $\text{KO}^+\text{Bu}$  (10mg) and Iminine (0.82g) was stirred for 24 hours under  $\text{H}_2$  gas (15 bar). The NMR showed 100% conversion.

Cat = RuHCl(R-binap)(R,R-*open*)

Cat = 5 mg, Iminine = 0.73g,  $\text{KO}^+\text{Bu}$  = 10mg  
 $\text{H}_2$  = 15 bar.

100% conversion in 24 hours.

Cat = RuHCl(R,R-*oppcap*)(R,R-*cycl*)

Cat = 3 mg, Iminine = 0.28g,  $\text{KO}^+\text{Bu}$  = 10mg  
 $\text{H}_2$  = 15 bar.

Complete conversion in 24 hours.

Cat = RuHCl(R,R-*oppcap*)(R,R-*open*)

Cat = 5 mg, Iminine = 0.86g,  $\text{KO}^+\text{Bu}$  = 10mg  
 $\text{H}_2$  = 15 bar.

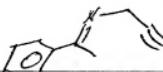
Complete conversion in 24 hours.

$\text{NH}_2$

Preparation of  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

The propargylamine prepared from reduction of the imine was used. The procedure follows the one reported by Banerjee et al. (Tetrahedron Lett. 1999, 40, 767-770).

A mixture of  $\text{TiCl}_3$  (1.54 g) and lithium metal (231 mg) was refluxed for 3 hours under argon in THF (20 ml). A solution of the propargylamine (500 mg) in THF (5 ml) was added to the reagent and stirred for 1 hour at room temperature. The reaction mixture was diluted with hexane/ethyl acetate (70/30) and filtered through celite. The filtrate was washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under vacuum. The crude product was purified by chromatography to yield benzylamine (245 mg).

Hydrogenation of 

Cat = RuHCl(R-bings)(R,R-Cycl)

A mixture of the catalyst (5mg),  $\text{KO}^+\text{Ba}^-$  (10mg) and imine (0.89g) in  $\text{C}_6\text{D}_6$  (2ml) was stirred under  $\text{H}_2$  gas (30 bar) for 24 hours. NMR showed 97% conversion.  
e.e. = 78% (S)

Cat = RuHCl(R-bings)(R,R-open)

Cat = 5mg, Imine = 0.80g,  $\text{KO}^+\text{Ba}^-$  = 10mg  
 $\text{H}_2$  = 30 bar.

NMR showed 100% conversion.  
e.e. = 67% (S)

Cat = RuHCl(R,R-dppm)(R,R-cycl)

Cat = 5mg, Imine = 1.07g,  $\text{KO}^+\text{Ba}^-$  = 10mg  
 $\text{H}_2$  = 30 bar.

100% conversion. e.e. = 52% (S)

Cat = RuHCl(R,R-dppm)(R,R-open)

Cat = 5mg, Imine = 0.94g,  $\text{KO}^+\text{Ba}^-$  = 10mg  
 $\text{H}_2$  = 30 bar.

NMR showed 100% conversion.  
e.e. = 51% (S).

Preparation of [O]

Prepared from propargylamine derived from hydrogenation of imine.  
 (Banerji et al, Tetrahedron Lett. 1989, 40, 767-770).

A solution of the propargylamine<sup>(500 mg)</sup> was added to the LVT reagent and the resulting mixture was stirred for 2 hours at room temperature. The reaction mixture was diluted with Lesches/ethyl acetate (70/30) and filtered through celite. The crude product was purified using chromatography to yield the amine. Yield = 290 mg.

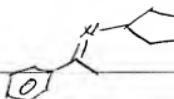
Preparation of [O]

NH<sub>2</sub> S-MeAmpy

The ligand was prepared using the reported literature procedure  
 Inorg. Synth. 1998, 32, 70.

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[REDACTED] Hydrogenation of



Cat = RuHCl(R-bipy)(R,R-cycl)

A mixture of the catalyst (5 mg), ~~was added~~  
Tinire (0.19 g),  $\text{KO}^+\text{Bu}$  (20 mg) in  $\text{C}_6\text{D}_6$  (2 mL)  
was stirred under hydrogen (50 bar) for  
36 hours. The NMR showed 94 %  
conversion of the imine to amine.

Cat = RuHCl(R-bipy)(R,R- $\alpha$ -pen)

Cat = 5 mg, Tinire = 0.19 g,  $\text{KO}^+\text{Bu}$  = 20 mg  
 $\text{H}_2$  = 50 bar.

The NMR showed 83 % conversion  
after 36 hours.

Cat = RuHCl(R,R-dppad)(R,R-cycl)

Cat = 5 mg, Tinire = 0.25 g,  $\text{KO}^+\text{Bu}$  = 20 mg  
 $\text{H}_2$  = 50 bar.

97 % conversion in 36 hours.

Cat = RuHCl(R,R-dppad)(R,R- $\alpha$ -pen)

Cat = 5 mg, Tinire = 0.22 g,  $\text{KO}^+\text{Bu}$  = 20 mg  
 $\text{H}_2$  = 50 bar.

95 % conversion on 36 hours.

Hydrogenation of [O]

Cat = RuHCl(*R*-binap)(*R,R*-cycl)

Cat = 5 mg, Tinire = 0.16 g,  $\text{KO}^+\text{Bu}$  = 30 mg  
 $\text{H}_2$  = 50 bar,  $\text{C}_6\text{D}_6$  = 2 ml.  
~~92 %~~ conversion in 36 hours.

Cat = RuHCl(*R*-binap)(*R,R*-dpen)

Cat = 5 mg, Tinire = 0.15 g,  $\text{KO}^+\text{Bu}$  = 30 mg  
 $\text{H}_2$  = 50 bar,  $\text{C}_6\text{D}_6$  = 2 ml.  
 89 % conversion in 36 hours.

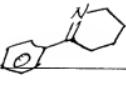
Cat = RuHCl(*R,R*-dppach)(*R,R*-cycl)

Cat = 5 mg, Tinire = 0.20 g,  $\text{KO}^+\text{Bu}$  = 30 mg  
 $\text{H}_2$  = 50 bar,  $\text{C}_6\text{D}_6$  = 2 ml.  
 97 % conversion in 24 hours.

Cat = RuHCl(*R,R*-dppach)(*R,R*-dpen)

Cat = 5 mg, Tinire = 0.17 g,  $\text{KO}^+\text{Bu}$  = 30 mg  
 $\text{H}_2$  = 50 bar,  $\text{C}_6\text{D}_6$  = 2 ml.  
 93 % conversion in 24 hours.

Hydrogenation of



Cat = RuHCl(R-binap)(R,R-cycl)

Cat = 3mg, Imine = 0.18g, KOTBu = 20mg  
H<sub>2</sub> = 50 bar, C<sub>6</sub>D<sub>6</sub> = 2 ml.

82% conversion in 36 hours.

Cat = RuHCl(R-binap)(R,R-dpen)

Cat = 3mg, Imine = 0.16g, KOTBu = 20mg  
H<sub>2</sub> = 50 bar, C<sub>6</sub>D<sub>6</sub> = 2 ml

76% conversion on 36 hours.

Cat = RuHCl(R,R-dppm)(R,R-cycl)

Cat = 3mg, Imine = 0.22g, KOTBu = 20mg  
H<sub>2</sub> = 50 bar, C<sub>6</sub>D<sub>6</sub> = 2 ml.

94% conversion in 36 hours.

Cat = RuHCl(R,R-dppm)(R,R-dpen)

Cat = 3mg, Imine = 0.19g, KOTBu = 20mg  
H<sub>2</sub> = 50 bar, C<sub>6</sub>D<sub>6</sub> = 2 ml.

88 conversion in 36 hours.

[REDACTED] Hydrogenation of [REDACTED]

Catalyst = RuHCl(*R*-binap)(oscam)

A mixture of the catalyst (5 mg), KOTBu (10 mg) and acetophenone (1.0 g) in *CDCl*<sub>3</sub> was stirred for 24 hours under hydrogen (10 bar). The NMR showed 100% conversion to the alcohol (e.e. = 70% (S)).

Cat = RuHCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(oscam)

Cat = 5 mg, KOTBu = 10 mg, *CDCl*<sub>3</sub> = 2 mL  
H<sub>2</sub> = 10 bar, acetophenone = 1.0 g.

100% conversion in 24 hours.

Cat = RuHCl(*R,R*-dppach)(oscam)

Cat = 5 mg, KOTBu = 10 mg, acetophenone = 1.0 g, H<sub>2</sub> = 10 bar

100% conversion in 24 hours.

Hydrogenation of



Three test tubes were used for the simultaneous hydrogenation of benzyl acetone. Each tube contains (1) 5 mg catalyst (2) 1g acetophenone (3) 10 mg  $\text{KO}^+\text{Bu}$  (4) 2ml  $\text{C}_6\text{D}_6$ . The tubes were placed in a Parr reactor and a magnetic stirrer placed in each. The pressure ( $\text{H}_2$ ) was adjusted to 10 bar and stirred for 24 hours.

$\text{RuCl}(\text{PPh}_3)_2(\text{OAc})$  - 100 %

$\text{RuHCl}(\text{n}-\text{binap})(\text{OAc})$  - 100 %

$\text{RuHCl}(\text{R},\text{R}-\text{approach})(\text{OAc})$  - 100 %

Hydrogenation of



Test tubes were used for simultaneous hydrogenation. (1) 10 mg catalyst (2) 10 mg  $\text{KO}^+\text{Bu}$  (3) 0.5 g acetone (4) 2ml  $\text{C}_6\text{D}_6$ , pressure = 30 bar ( $\text{H}_2$ ).

The mixtures were stirred for 24 hours.

$\text{RuHCl}(\text{PPh}_3)_2(\text{OAc})$  - 87 %

$\text{RuHCl}(\text{n}-\text{binap})(\text{OAc})$  - 100 %

$\text{RuHCl}(\text{R},\text{R}-\text{approach})(\text{OAc})$  - 100 %

## Hydrogenation of

Tgt tubes were used for simulaneous reactions. Each contained:

(1) 10 mg cat. (2) 0.5 g imine (3) 10 mg  $\text{HOTBu}$  (4)  $\text{C}_6\text{D}_6$  - ml.  $\text{H}_2 = 10$  bar.

The mixtures were stirred for 24 hours.

$\text{RuHCl}(\text{pph}_3)_2(\text{oicam})$  - 88 %

$\text{RuHCl}(\text{R}-\text{binap})(\text{oicam})$  - 100 %

$\text{RuHCl}(\text{R},\text{R}-\text{dppach})(\text{oicam})$  - 100 %.

## Hydrogenation of

Each Tgt tube contained:

(1) 10 mg cat. (2) 0.5 g imine (3)  $\text{HOTBu}^n$   
 $= 20$  mg (4)  $\text{C}_6\text{D}_6 = 2$  ml.  $\text{H}_2 = 30$  bar.  
 After 36 hours:

$\text{RuHCl}(\text{pph}_3)_2(\text{oicam}) = 22 \%$

$\text{RuHCl}(\text{R}-\text{binap})(\text{oicam}) = 18 \%$

$\text{RuHCl}(\text{R},\text{R}-\text{dppach})(\text{oicam}) = 27 \%$ .

Preparation of  $\text{Cl}-\text{N}(\text{Tris})_2$

$\text{NEt}_3$  (400 ml) was added to a mixture of 2-chloroethylamine hydrochloride (100g) in  $\text{CH}_2\text{Cl}_2$  (1.5 L) and the mixture stirred vigorously for 2 hours under argon. A solution of  $\text{TiNCl}$  (240 ml) in  $\text{CH}_2\text{Cl}_2$  (400 ml) was then added slowly and the resulting mixture stirred vigorously at room temperature for 12 hours. The mixture was filtered, and the solids washed with 800 ml of  $\text{CH}_2\text{Cl}_2$ . The combined filtrate was evaporated to remove the solvents and hexane (500 ml) added. The mixture was stirred for 2 hours, then filtered, and the filtrate evaporated under reduced pressure to give the product as a pale yellow liquid. Yield = 198.3 g.

Preparation of  $\text{PdHCl}(\text{CpPh}_3)_2(5\text{-MeAmpy})$

$\text{THF}$  (5ml) was added to a mixture of  $\text{PdHCl}(\text{CpPh}_3)_2$  (200 mg) and 5-MeAmpy (80 mg) and the resulting solution was stirred for 2 hours under argon. Hexanes (20 ml) was added and the yellow-green solid was filtered, washed with hexanes and dried under  $\text{vacuum}$ . Yield = 152 mg.

[REDACTED] Preparation of Ph<sub>2</sub>P(NH<sub>2</sub>)

A THF (120 ml) solution of chlorodiphenylphosphine (60 g) was added slowly to a suspension of lithium granules (6.0 g) in THF (100 ml) and the mixture stirred for 3 days at room temperature. The mixture was filtered through a sintered glass fit to remove excess lithium and the filtrate cooled to -40°C. A solution of  $\mu,\mu$ -bis(trimethylsilyl)ethylamine (62 g) in 200 ml THF was slowly added. The resulting suspension was warmed to R.T. and 50 ml of the mixture was refluxed for 1 hour. After cooling to R.T. 50 ml of water was added. The mixture was refluxed for one hour, cooled to R.T. and the aqueous layer was removed. Another 50 ml of water and 50 ml of hexanes was added and the mixture was refluxed for 4 hours, then cooled to R.T. The aqueous layer was removed and the mixture was evaporated to give the crude aminophosphine. This was purified by vacuum distillation. Yield = 38.29.

~~[REDACTED]~~ Hydrogenation of ~~TO~~

4 test tubes were used to simultaneously hydrogenate acetophenone under the same conditions using 4 amino pyridine catalysts. Each tube contained:

Cat = 5 mg,  $\text{H}_2\text{O}^\circ\text{Cu} = 10 \text{ mg}$ , Acetophenone - 1.0 g,  $\text{C}_6\text{D}_6 = 7 \text{ ml}$

The tubes were placed in a Parr pressure reactor (10 bar) and stirred for 12 hours.

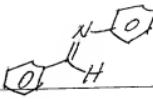
RuHCl( $\text{pph}_3$ )<sub>2</sub>(S-MeAmpy) - 100 %, 47 % (R)

RuHCl( $\text{pph}_3$ )<sub>2</sub>(Ampy) - 100 %

RuHCl( $\text{B}-\text{pinac}$ )(S-MeAmpy) - 100 %, 72 % (R)

RuHCl( $\text{B},\text{B}'-\text{dppach}$ )(S-MeAmpy) 100 %, 59 % (R)

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Hydrogenation of 

Reactions were done in 4 test tubes.

(1) Cat = 5 mg, Tetrade = 0.5 g, KOBa = 10 mg, CpOB = 2 ml, H<sub>2</sub> = 10 bar.

Reaction mixtures were stirred for 24 hours.

RuHCl(ppy) <sub>3</sub> (S-Me Ampy)	- 100 %
RuHCl(ppy) <sub>3</sub> (AcPy)	- 100 %
RuHCl(S-bipy)(S-Me Ampy)	- 79 %
RuHCl(S,S-dppad)(S-Me Ampy)	- 100 %